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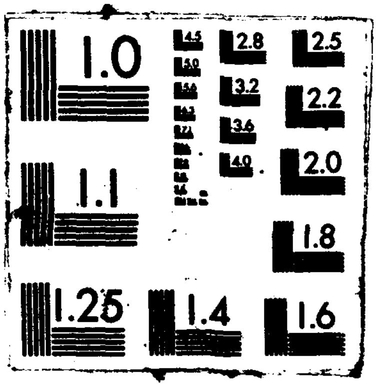
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CONTACT NOISE IN SODIUM β'' ALUMINA

by

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CONTACT NOISE IN SODIUM β" ALUMINA

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May 1987

ABSTRACT

Contact noise in sodium β"alumina cells has been studied by voltage fluctuation measurements at frequencies 10^{-4} to 3×10^{4} Hz in the presence and absence of current. A propylene carbonate solution of NaI forms a low noise contact with β"alumina ceramic electrolyte. The noise spectra for aqueous solution of $NaNO_3$, silver amalgam and newly prepared mercury electrodes, however, show excess noise at low frequencies and exhibit f^{-2} spectra that suggests nonequilibrium reactions occur at the interface. The current noise of both the aqueous and propylene carbonate solution electrodes displays $f^{-1.5}$ dependence characteristic of diffusion noise.

I. INTRODUCTION

Electrical noise spectra in the presence or absence of current reflect the ion transport and exchange or ion-electron transfer kinetics in an ion conducting system. Under nonequilibrium conditions, the voltage and current fluctuations often provide information about ion diffusion in bulk electrolyte, surface ion exchange, interfacial charge transfer and electrochemical reactions. On the other hand, the voltage fluctuation data at equilibrium can lead to an understanding of the dynamic process of charged species without net ion and charge transfer. Particularly, equilibrium noise measurements are of special interest in superionic solids and devices since it displays transport and transfer effects of an ionic system without external perturbation. Such perturbations sometimes are most undesirable for systems that have low electrolytic stability.

Recent studies on noise spectra of sodium[1-3] and ion exchanged[4,5] β"aluminas have shown that conductivity fluctuations in both the ceramic and single crystal substances should be attributed to the diffusion noise of the mobile ions and the greater noise and stronger temperature dependance than predicted by the standard expression for diffusion noise could be supposed to arise from correlation effects of the mobile ions. In addition, the excess noise level and noise relaxations observed in the low frequency portion are accounted for by non-equilibrium electrochemical reactions. It can be seen from a comparison of various cell configurations that the voltage fluctuations at electrical contacts to β"alumina exhibit a rich variety of characteristics. Further investigation on contact noise should be helpful to reveal the physical and chemical processes occur at the interface between electrolyte and electrode.

II. EXPERIMENTAL PROCEDURE

Cells with two- and four-terminal electrodes were prepared from commercial sodium β"alumina electrolyte[6]. The cell preparation technique is essentially identical to ref. 3, Square ceramic samples of 1x1x0.2 cm were sealed with epoxy cement into the sides of four plastic tubes holding liquid electrodes to provide diagonally opposing corner current terminals and transverse potential electrodes. Two-terminal cells were built from rectangular ceramics of 1x0.5x0.4 cm. In special cases, cells with unequal contact areas were prepared in the two-terminal compartments for identifying the nature of noise at a given contact. The liquid electrodes were formed by 0.5 M NaI propylene carbonate solution (PC), 2 M $NaNO_3$ aqueous solution, mercury and silver amalgam.

Noise voltages were measured in a set-up consisting of a PAR 113 preamplifier, external filter and a digital FFT analyzer[7]. Frequency scans cover 10^{-4} to 3×10^{4} Hz. Log-log noise spectra are plotted by an on-line Apple IIe computer.

III. NOISE RESULTS AND DISCUSSION

1. NaI PC solution/Na β"alumina

Typical noise spectra of the PC electrode are shown in Figure 1. In the absence of current, the high frequency noise is approximately in agreement with the Nyquist noise corresponding to the resistance of bulk β"alumina electrolyte. Low frequency noise of the cell is comparable to that of PAR 113 preamplifier that indicates small contact noise between β"alumina and propylene carbonate. Excess noise voltages were observed accompanying current flow. The log-log noise plot gives a slope of -1.5, and the noise voltages increase with the current squared in the observed range of current intensity. The spectral shape is characteristic of diffusion dominated noise. After passing current, the PC electrode retained its original low noise level. The low noise observed before and after electricity flow indicates a good contact and little electrochemical changes at the β"alumina-propylene carbonate solution interface.

2. $NaNO_3$ aqueous solution/sodium β"alumina contact

Because of the low noise of the propylene carbonate electrode, cells having one propylene carbonate solution contact and the other contact provided by sodium nitrate aqueous solution were formed. In these cells the noise observed arises from only the latter electrode, since sodium iodide solution contact is low noise.

Illustrated in Figures 2 and 3 are the noise spectra of the cell NaI PC solution/β"alumina/$NaNO_3$ aqueous solution. In addition to Nyquist noise, high contact noise in comparison with the NaI(PC)/NaI(PC) cell is detected at frequenices below 100 Hz, and the spectral pattern shows f^{-2} dependence. After current flow, the low frequency noise decreases.

In the presence of current direction chosen to inject protons or sodium ions into the β"alumina from the aqueous electrode, the noise level increases and the spectral shape changes to $f^{-1.5}$, suggesting that bulk diffusion noise dominates. A higher slope of -1.8 at 50 μA current in Figure 3 may arise from

two overlapped noise effects associated with the ion diffusion and ion exchange processes. In contrast to zero current spectra, the current noise levels increase with accumulated charge passage, as demonstrated in Figure 3.

The ion exchange between sodium ions and hydrated protons at the β"alumina surface may reasonably account for the f^{-2} Lorentzian dependence of voltage fluctuations observed in the experimental noise spectra in the absence of current. The decrease of low frequency noise may be related to slowing down the rate of ion exchange as the concentration of protons increases due to charge accumulation since the direction of current helps the protons to enter into the β"alumina lattice. On the other hand, the increase in current noise after passage of electricity may be simply explained by the decrease of carrier concentration because of the ion exchange even though the diffusion coefficient might be slightly decreased also.

3. Hg/β"alumina and Ag amalgam/sodium β"alumina contacts

Figures 4 and 5 give the contact noise spectra of NaI(PC)/sodium β"alumina/silver amalgam and NaI(PC)/sodium β"alumina/mercury cells respectively. Both cells exjhibit a f^{-2} dependent spectral shape at low frequencies, which indicates non-equilibrium chemical reactions. As shown previously [3], a relaxation plateau is also found around 100 Hz in both cells. A non-equilibrium reaction between the sodium β"alumina and silver amalgam responsible for this noise process may arise from interaction between mercury and the sodium ions in β"alumina, since this interfacial process is observed at mercury-β"alumina contact as well. This interpretation must await additional data. However, one possible noise source may be supposed to be associated with forming sodium-mercury organized connections in the liquid amalgam, as has been proposed in the structure modeled calculations[8-10] for explaining the extremely low activity coefficient of sodium. Experiments currently in progress in this laboratory show that the 100 Hz noise relaxation level in the mercury/mercury cell increases and shifts towards low frequencies with decreasing temperature.

IV. CONCLUSIONS

1. Propylene carbonate forms a low noise contact with β"alumina and such a low noise electrode can be used to observe the noise generated by a second contact to the cell.

2. Aqueous solution electrodes display f^{-2} dependent noise in the absence of current, suggeting an interfacial non-equilibrium reaction. The zero-current noise decreases with accumulated charge passage.

3. In the presence of current, the cells with propylene carbonate and aqueous solution electrodes show diffusion dominated noise.

4. Preliminary investigation on mercury/β"alumina and silver amalgam/β"alumina contacts indicates interfacial reactions having a characteristic relaxation at 100 Hz.

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* On leave from Shanghai Institute of Ceramics, Chinese Academy of Sciences.

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FIGURE CAPTIONS

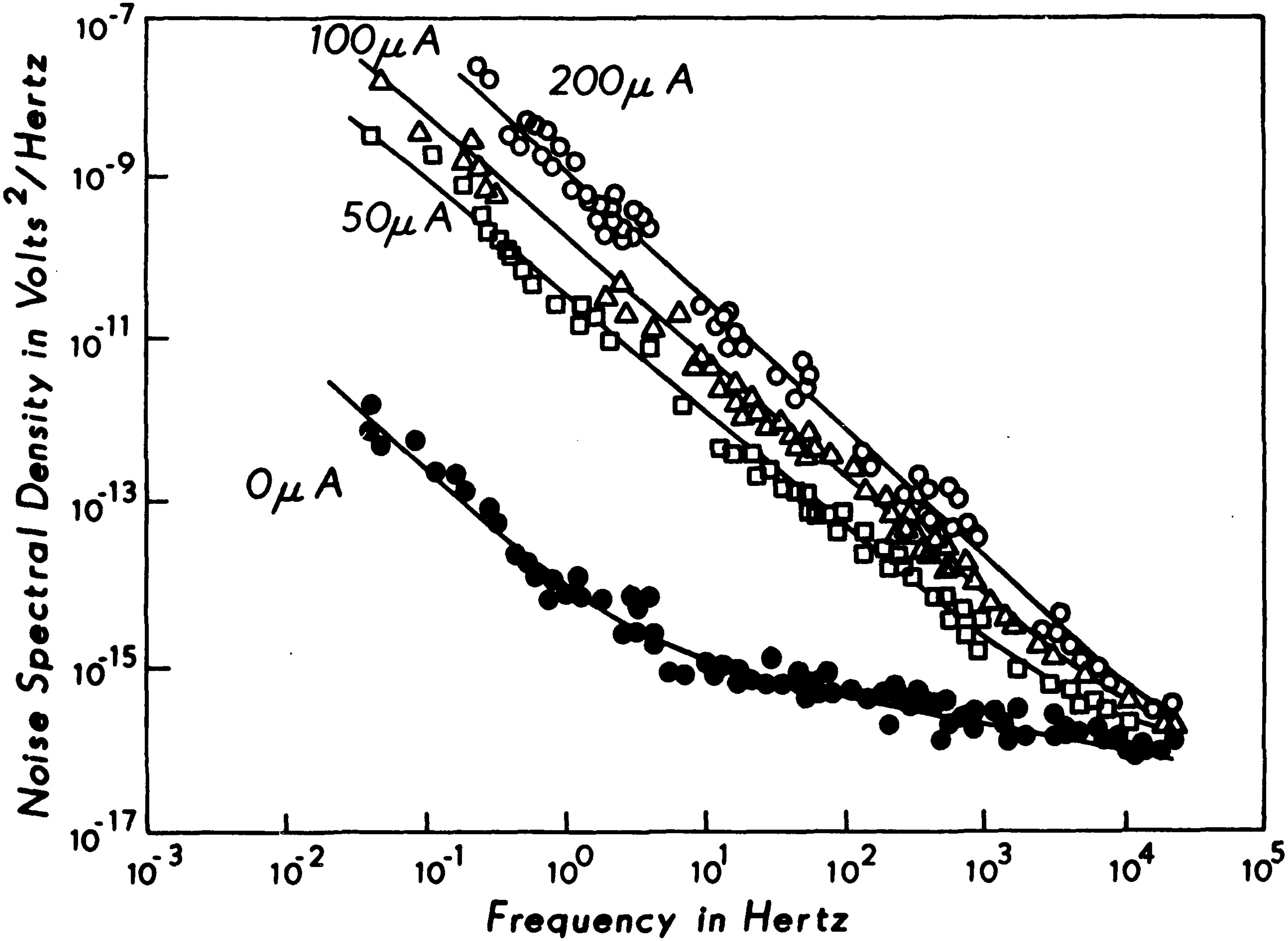
Figure 1. Contact and current noise in NaI PC solution/sodium β"alumina/ NaI PC solution cell.

Figure 2. Contact and current noise of NaI PC solution/sodium β"alumina/ $NaNO_3$ aqueous solution cell.

Figure 3. Contact and current noise in NaI PC solution/sodium DbE"alumina/ $NaNO_3$ aqueous solution cell, showing decreased zero current noise and increased current noise after passing 2.8 Coulombs.

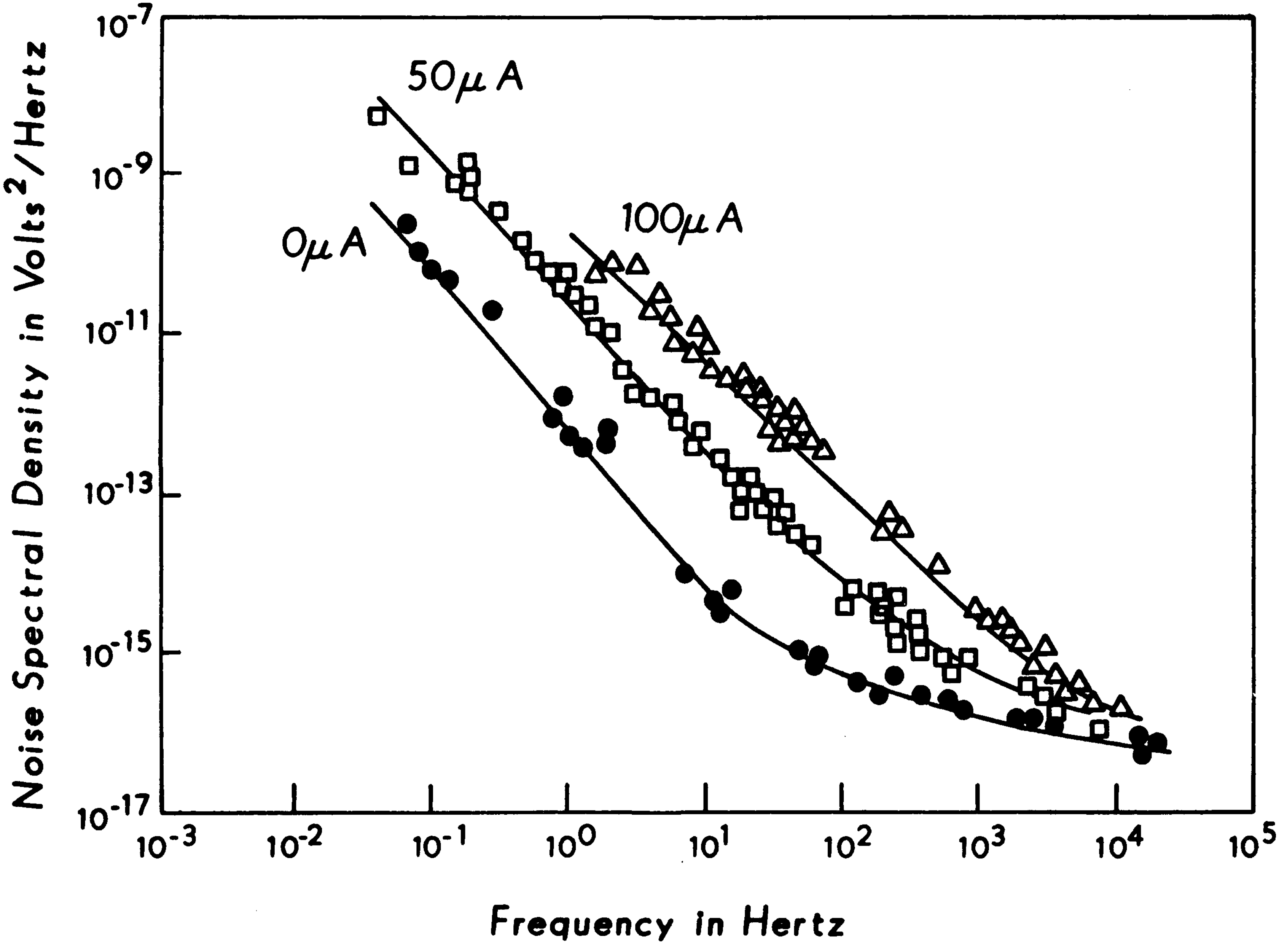
Figure 4. Contact noise of silver amalgam sodium β"alumina electrode.

Figure 5. Contact noise of mercury/sodium β"alumina electrode.



100μA
200μA
50μA
0μA
Noise Spectral Density in Volts²/Hertz
Frequency in Hertz
10⁻⁷
10⁻⁹
10⁻¹¹
10⁻¹³
10⁻¹⁵
10⁻¹⁷
10⁻³
10⁻²
10⁻¹
10⁰
10¹
10²
10³
10⁴
10⁵

Figure 1



Noise Spectral Density in Volts²/Hertz
10-7
10-9
10-11
10-13
10-15
10-17
50μ A
100μ A
0μ A
10-3
10-2
10-1
100
101
102
103
104
105
Frequency in Hertz

Figure 2

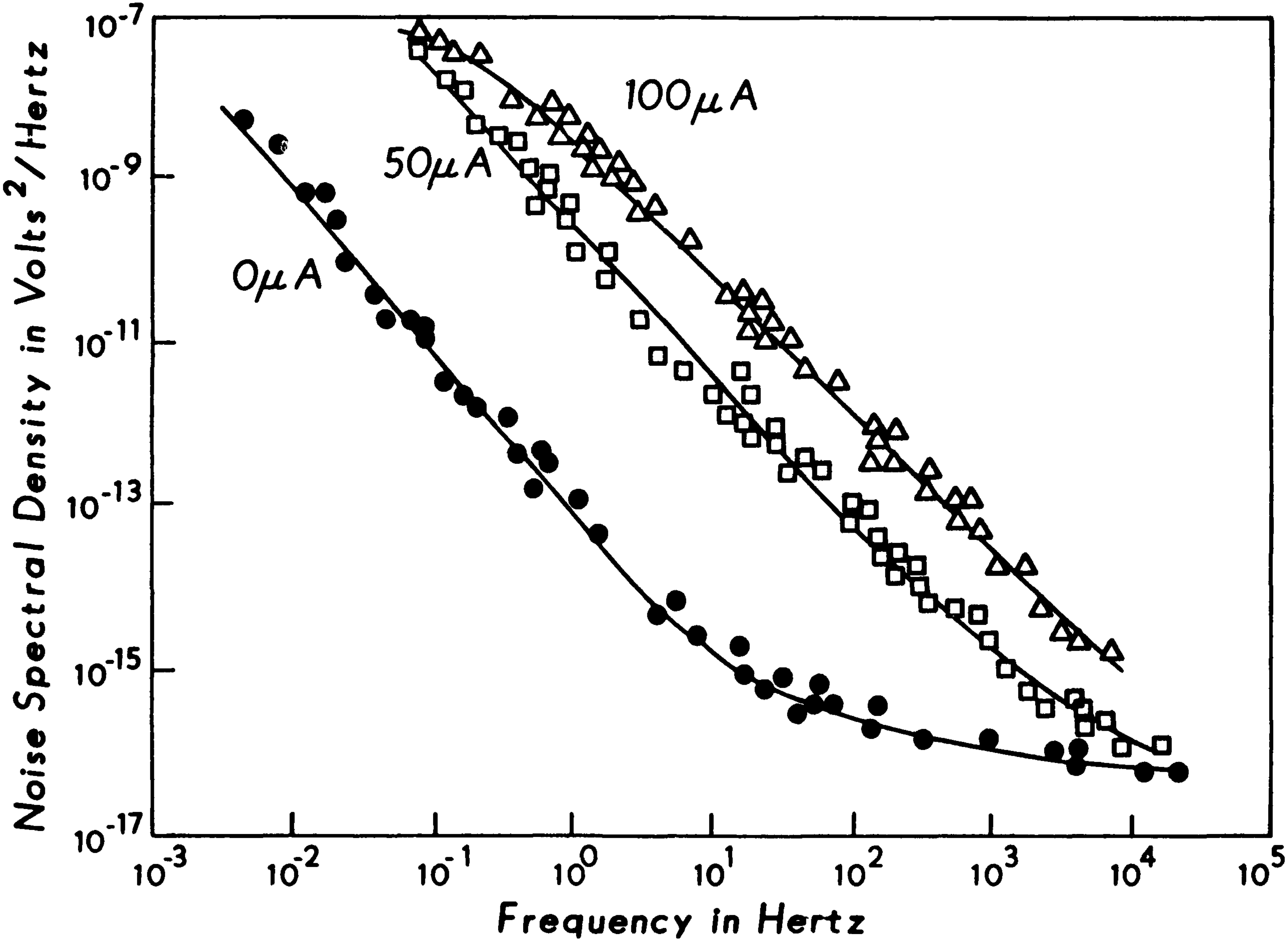
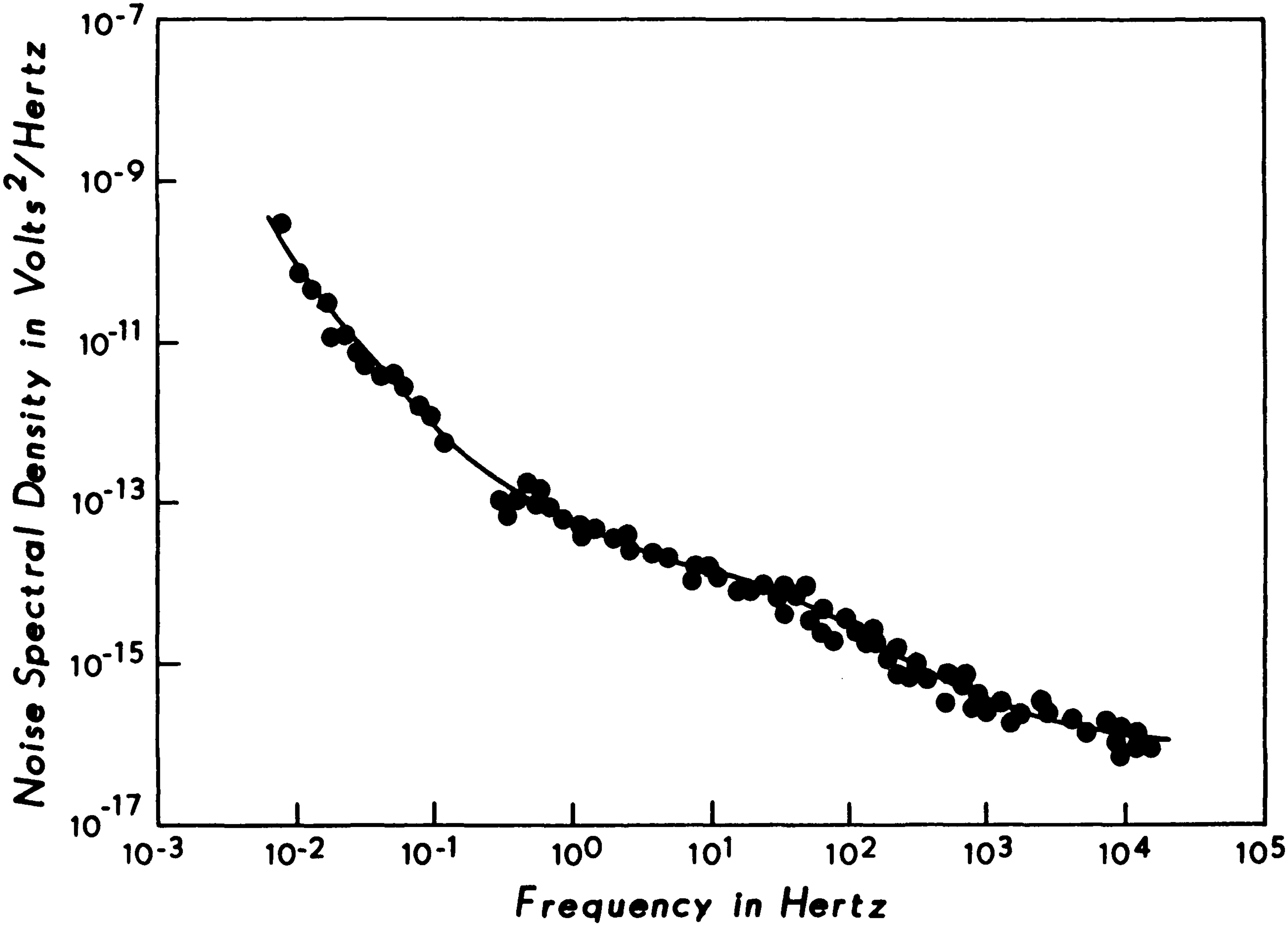
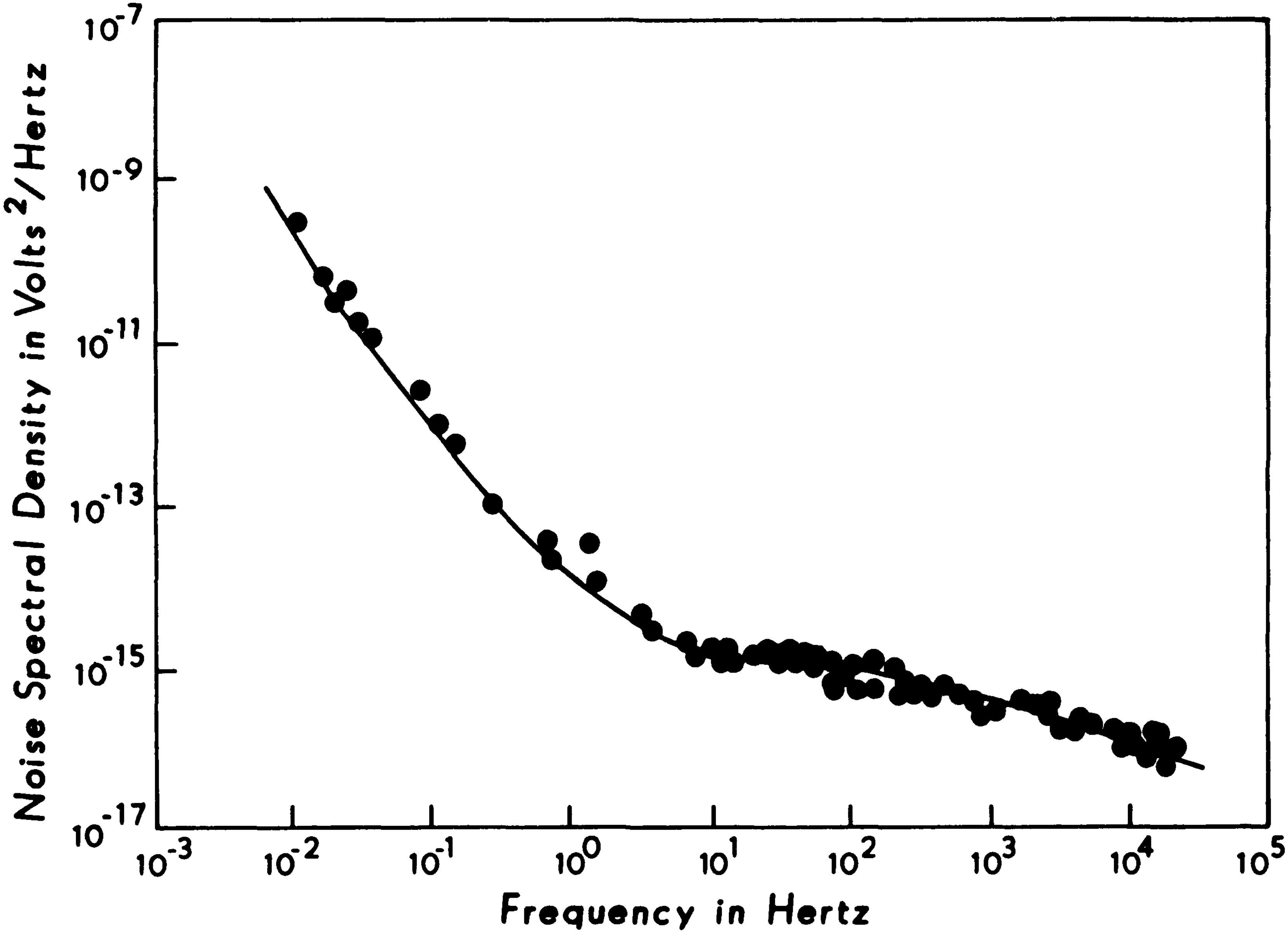

Noise Spectral Density in Volts ^{2}/Hertz
10^{-7}
10^{-9}
10^{-11}
10^{-13}
10^{-15}
10^{-17}
100 μA
50 μA
0 μA
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
Frequency in Hertz

Figure 3



Noise Spectral Density in Volts²/Hertz
10-7
10-9
10-11
10-13
10-15
10-17
10-3
10-2
10-1
100
101
102
103
104
105
Frequency in Hertz

Figure 4



Noise Spectral Density in Volts²/Hertz
10^{-7}
10^{-9}
10^{-11}
10^{-13}
10^{-15}
10^{-17}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
Frequency in Hertz

Figure 5

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